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June 29, 2006

Jornal of Geophysical Research- Atmospheres

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Abstract

Particulate matter aerosols contribute to haze diminishing vistas and scenery at National Parks and Wilderness Areas within the United States. To increase understanding of the sources of carbonaceous aerosols at these settings, the total carbon loading and $^{14}C/C$ ratio of PM 2.5 aerosols at nine IMPROVE (Interagency Monitoring for Protection Of Visual Environments) network sites were measured. Aerosols were collected weekly in the summer and winter at one rural site, two urban sites, five sites located in National Parks and one site located in a Wildlife Preserve. The carbon measurements together with the absence of ^{14}C in fossil carbon materials and the known $^{14}C/C$ levels in contemporary carbon materials were used to derive contemporary and fossil carbon contents of the particulate matter. Contemporary and fossil carbon aerosol loadings varied across the sites and suggest different percentages of carbon source inputs. The urban sites had the highest fossil carbon loadings that comprised around 50% of the total carbon aerosol loading. The Wildlife Preserve and National Park sites together with the rural site had much lower fossil carbon loading components. At these sites, variations in the total carbon aerosol loading were dominated by non-fossil carbon sources. This suggests that reduction of anthroprogenic sources of fossil carbon aerosols may result in little decrease in carbonaceous aerosol loading at many National Parks and rural areas.

Index Terms: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry.

Keywords: aerosols, PM 2.5, carbon-14, fossil carbon, contemporary carbon.

Introduction

National Parks and Wilderness Areas within the United States possess dramatic vistas and scenery, which can be diminished by haze causing discoloration and loss of texture and visual range. The impact of PM 2.5 (particles with mean mass aerodynamic diameter $\leq$ 2.5 μm) aerosols on visibility, as well as compliance with the Environmental Protection Agency's (EPA) regional haze regulations [*U.S. Environmental Protection Agency,* 1997; *U.S. Environmental Protection Agency*, 1999,] is a growing concern. To establish current visibility conditions, track changes in visibility and determine causal mechanisms for visibility impairment in National Parks and Wilderness Areas, the IMPROVE (Interagency Monitoring for Protection Of Visual Environments) program (http://vista.cira.colostate.edu/improve/) has conducted an extensive long term monitoring campaign across the United States over the past twenty years.

In general, the largest mass fractions of the PM 2.5 aerosol at IMPROVE network sites are sulfates and organics [*Malm et al.,* 2004]. Carbon containing aerosols are the largest single component of PM 2.5 aerosol mass at many IMPROVE sites in the western United States where it can contribute up to fifty percent of the fine aerosol mass [*Malm et al.,* 2004]. Particulate carbonaceous material originates from anthropogenic and biogenic sources either directly emitted into the atmosphere or formed as secondary organic aerosols (SOA) in the atmosphere from precursor gases. The diverse sources and atmospheric processing result in a complex mixture of many different compounds. The presence and total concentration of carbonaceous particulate matter is simple to confirm and quantify from ambient aerosol samples; for example, carbon-containing compounds can be oxidized to CO_2 gas over an appropriate temperature range. The challenge is in attempting to speciate the aerosol carbon in order to understand not

only its composition but also to elucidate the sources that contribute to carbonaceous particulate matter.

Significant advances in carbonaceous aerosol source apportionment have been made using molecular tracers in chemical mass balance (CMB) receptor models [*Chow and Watson,* 2002 and references therein]. With such approaches, unique molecules (or molecular tracers) are identified for a source and the relative abundance of these species in the ambient samples are used to deduce fractional contributions from each profiled source. While compound specific analysis has proven its value in a variety of atmospheric chemistry studies, numerous source profiles are often needed to apportion a significant amount of the ambient aerosols. In addition, the CMB model generally does not account for SOA that can be a substantial portion of the organic aerosol. Due to the lack of sufficient source profiles and presence of SOAs the CMB approach often suffers from only being able to characterize approximately 30% or less of the total organic mass [*Rogge et al.,* 1993]

Recently, ^{14}C measurements have been used to estimate the relative contributions of fossil fuels and biogenic aerosols to the aerosol carbon loading [*Lemire et al.,* 2002; *Bench and Herckes,* 2004; *Lewis et al.,* 2004; *Szidat et al.,* 2004; *Tanner et al.,* 2004; *Lewis and Stiles,* 2006]. ^{14}C determinations offer a unique possibility for mass weighted source apportionment of carbonaceous aerosol particles due to a direct distinction between contemporary and fossil carbon. ^{14}C is present at a small but approximately constant level in living (or contemporary) materials but absent in fossil fuels. Moreover, ^{14}C is a robust "tracer", retaining its identity throughout any chemical transformations. Consequently, a ^{14}C measurement performed on a particulate matter aerosol sample provides a means of quantitatively distinguishing the relative contributions of fossil and contemporary carbon sources (although they are frequently more

loosely referred to as anthroprogenic and biogenic carbon [*Lemire et al.,* 2002; *Lewis et al.,* 2004]) to the total carbon mass loading. ^{14}C measurements provide an alternative source apportionment approach that is complementary to methods using molecular tracers. While ^{14}C measurements cannot distinguish specific sources without coupling to sample speciation methods, they are not impacted by an inability to account for a significant fraction of the aerosol carbon mass.

^{14}C measurements conducted during the summer of 2002 at the IMPROVE site on Turtleback Dome, Yosemite National Park [*Bench and Herckes,* 2004] revealed that the PM 2.5 aerosol fossil carbon loading was relatively constant averaging 0.7 $\mu g/m^3$ and independent of the PM 2.5 total carbon content that varied from 2.5 to 10 $\mu g/m^3$. Conversely, the contemporary carbon content varied in direct proportion to the total carbon content of the PM 2.5 aerosol. During the study, visibility at the sampling site was periodically impaired due to significant contributions from smoke derived from wild fires and at least some of the variability in the contemporary carbon loading arose from this source. Although the average PM 2.5 carbon mass loading was higher than the historical average [*Bench and Herckes,* 2004], the data suggested that fossil carbon aerosols might comprise a relatively small fraction of the carbon aerosol mass loading at Yosemite National Park.

Here, measurements of total carbon loading and $^{14}C/C$ ratio of PM 2.5 aerosols collected at nine IMPROVE network sites are reported. These data are used to determine fossil and contemporary carbon aerosol loadings across a diverse range of National Parks located throughout the contiguous United States.

Methods

Sample Collection

Here PM 2.5 aerosols collected at nine IMPROVE network sites are reported. Table 1 details the site names; IMPROVE codenames for the sites and site descriptions. The sites located at Brigantine National Wildlife Refuge, Mount Rainier National Park, Puget Sound, Great Smoky Mountains National Park, and Proctor Maple Research Facility, were sampled from June through August 2004 and December 2004 through February 2005. The sites located at Grand Canyon (Hance camp), Phoenix, Rocky Mountain National Park and Tonto National Monument were sampled from June through August 2005 and December 2005 through February 2006. Figure 1 shows the location of the sites.

Samples were collected using Thermo Anderson Total Suspended Particulate (TSP) Hi-Vol samplers with SA-230-F impactor plates as previously described [*Bench and Herckes,* 2004]. With the exception of the Phoenix, Arizona site, one sampler was used at each site. A second sampler, placed approximately three meters from the sampler used for the summer 2005 sampling season, was employed at Phoenix during the winter 2005/2006 sampling season to assess reproducibility of the sampling and measurement methodology. All samplers were operated at a volumetric flow of 40 CFM to yield a PM 2.5 sample on a 20 cm x 25 cm quartz fiber filter (Gellman QM-A) per sampling period. The quartz filters were pre-fired by baking at 600^0 C for 12 hours and stored in sealed plastic bags prior to use. For each sampling period, a filter was exposed for up to six consecutive days (144 hours). Each week, sampling began at midnight Tuesday night and ended at midnight the following Monday night. Tuesday was a non-sampling day to allow for sampler servicing. Following deployment, quartz filters were immediately placed in re-sealable plastic bags.

Vehicle control filters were obtained by placing a quartz fiber filter in the sampler for ten minutes during sampler servicing on the Tuesday nearest the middle of a sampling month with the pump off. Following deployment, quartz filters were immediately placed in re-sealable plastic bags. Two or three vehicle control filters were collected at most sites for each sampling season. However, no vehicle controls were collected at Mount Rainer National Park and Brigantine National Wildlife Refuge in the winter of 2004/205. Likewise, no vehicle controls were collected at Phoenix in the summer of 2005.

Bagged filters were stored flat and unfolded in a cool dry, dark environment prior to monthly shipment to Lawrence Livermore National Laboratory (LLNL) for analysis.

Sample preparation and analysis

At LLNL, quartz fiber filters were processed as previously described for ^{14}C analysis [*Bench and Herckes,* 2004]. Briefly, areal samples of size 25 cm^2 (5 x 5 cm) were cut with a knife from the central region of each quartz filter. Each sample was directly combusted in vacuum at 900^{O} C with CuO oxidizer in a sealed quartz tube. CO_2 from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using an iron catalyst. $^{14}C/C$ ratios in the graphite samples were measured by accelerator mass spectrometry. The data were reported as a fraction of the Modern radiocarbon standard (fraction Modern or FM) [*Stuiver and Polach,* 1977]. A $\partial^{13}C$ value of -25 per mil was used [*Stuiver and Polach,* 1977] for all samples in order to correct the ^{14}C measurements for isotopic fractionation effects.

The average carbon loading and FM from the vehicle control filters within a season from each individual site were used to correct the site-specific aerosol laden filters to account for

endogenous carbon on the filters. When no vehicle controls were provided average values of carbon loading and FM obtained from the other vehicle control filters from the same sampling season were used. $^{14}C/C$ ratios from the aerosol-laden filters were corrected using:

$$R_a = R_m*L_m/(L_m-L_b) - R_b*L_b/(L_m-L_b) \qquad (1)$$

where R_a is the $^{14}C/C$ ratio of the PM 2.5 aerosol, R_m is the measured $^{14}C/C$ ratio of the PM 2.5 aerosol laden filter, L_m is the carbon mass of the analyzed region of the aerosol laden filter, L_b is the average carbon mass on the analyzed regions of the vehicle control filters, R_b, is the average $^{14}C/C$ ratio from the vehicle control filters, and $(L_m - L_b)$ is the PM 2.5 aerosol carbon mass. R_m, L_m and L_b have gaussian type analytical errors so uncertainties in R_a were derived from those in the measured quantities using standard error propagation relationships. Similar to a previous study [6] the mass of carbon on the vehicle control filters was typically small compared to that from aerosol laden filters so the resulting corrections to obtain the true aerosol carbon mass and FM on a filter were generally small.

For each aerosol laden sample, the PM 2.5 carbon aerosol loading (μg m^{-3}) was determined by extrapolating the corrected carbon mass from the analyzed section to the entire exposed surface of the filter, then taking into account the flow volume and the duration of sampling for the sample.

Derivation of contemporary and fossil carbon loadings

Contemporary and fossil carbon loading for each PM 2.5 aerosol sample were derived from the total carbon aerosol loading and associated FM using the absence of ^{14}C in fossil carbon

materials and the known $^{14}C/C$ levels in contemporary carbon materials as previously described [*Bench and Herckes,* 2004]. Briefly, if R_a is the $^{14}C/C$ ratio of a PM 2.5 aerosol sample and R_c is the $^{14}C/C$ ratio of the contemporary component, then the fraction F_c of the carbon that is derived from contemporary carbon is given by:

$$F_c = R_a/R_c \qquad (2)$$

because all of the ^{14}C must come from the contemporary fraction. The contemporary carbon aerosol loading is obtained from the product of F_c and the total carbon aerosol loading. The fossil carbon loading is the difference between the total and contemporary carbon aerosol loadings. Over the period from 1999 to 2003 the FM of contemporary samples slowly decreased from 1.11 to 1.07 Modern [*Levin and Kromer,* 2004]. Since 2003 the FM of contemporary samples has further decreased to around 1.05 Modern. For this study, R_c (the $^{14}C/C$ ratio of the contemporary component) was taken to be 1.08 +/- 0.06 Modern. This value corresponds to the average FM of contemporary material over the time period 1999 to 2005 with an uncertainty that corresponds to the difference between the maximum and minimum FM over this time period.

Statistical analysis

Potential differences in aerosol loading were assessed by unpaired two-tailed students t-tests. A significance level of < 0.05 was considered meaningful. A significance level between 0.05 and 0.1 was considered evidence of a possible trend, while a significance level of greater than 0.1 was considered to indicate no significant difference.

Results and Discussion

Reproducibility of the sampling and measurement methodology

Table 2 shows the fraction Moderns and total carbon loadings of PM 2.5 aerosols from the two collocated samplers at Phoenix. The uncertainties associated with the values reported in Table 2 are associated solely with the analytical measurement of total carbon and FM and do not account for uncertainties arising from sampler operation. A previous study [*Bench and Herckes,* 2004] that used identical sampling equipment and the same analytical procedures as reported here performed replicate analyses of total carbon mass and FM on PM 2.5 aerosol laden filters. The replicate analyses revealed consistency in both mass of carbon and associated FM to within the reported analytical measurement uncertainties [*Bench and Herckes,* 2004]. Because the data in Table 2 are from two collocated samplers, the comparison includes uncertainties arising from both sampler operation and analytical procedure. The degree of reproducibility of the data in Table 2 appears similar to that observed in other ^{14}C measurements of PM 2.5 aerosols from collocated samplers [*Lewis and Stiles,* 2006].

The average observed and analytical errors in fraction Moderns or total carbon loadings of PM 2.5 aerosols from two collocated samplers can be defined as:

$$Observed\ Error = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{([Y_i]-[X_i])/\sqrt{2}}{([Y_i]+[X_i])/2}\right)^2} \qquad (3)$$

where $[X_i]$ and $[Y_i]$ are the values of total carbon loading or fraction Modern from two collocated samplers X and Y and:

$$Analytical\ Error = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\frac{\left(E_{[X]_i}^2 + E_{[Y]_i}^2\right)/2}{\left(\left([X_i]+[Y_i]\right)/2\right)^2}} \qquad (4)$$

where $E_{[X]_i}$ and $E_{[Y]_i}$ are the analytical uncertainties errors in the measured values of total carbon loading or fraction Modern from the two collocated samplers..

The observed and analytical errors for the total carbon loading derived from the collocated samplers shown in Table 2 are 8.0% and 0.4 % respectively. Since the observed error includes uncertainties arising from both sampler operation and analytical procedure and assuming that these uncertainties are independent, the analytical error in the total aerosol carbon loading at Phoenix is small compared to uncertainties arising from sampler operation. A likely reason for the larger uncertainties arising from sampler operation is different flow rates for the two collocated samplers. The observed and analytical errors for the FM values derived from the collocated samplers shown in Table 2 are 1.3% and 0.7% and are not significantly different at the 0.05 level. This suggests that sources of uncertainty in sampler operation although affecting the uncertainty in aerosol carbon loading do not have as pronounced effect on the FM carbon values.

Summer and winter sampling at the nine sites

The fraction Moderns and total carbon loadings of PM 2.5 aerosols for the nine sites can be found in Tables A1 and A2 within the auxiliary material. Contemporary and fossil carbon loadings of the PM 2.5 aerosols derived from the carbon measurements at the nine sites are plotted against total carbon aerosol loading in Figure 2. Parameters for the linear least squares fits to the contemporary and fossil data for each graph in Figure 2 are shown in Table 3. Table 4

shows average PM 2.5 aerosol carbon loadings encountered each sampling season at all sites, together with assessments of the likelihood that aerosol carbon loadings for the summer and winter sampling seasons at each site are the same.

Sites sampled during 2004/2005

The data from Brigantine National Wildlife Refuge indicate that total, contemporary and fossil aerosol carbon loadings do not vary significantly between the two seasons. Although the carbon aerosols at Brigantine may be influenced by nearby Atlantic City, the total carbon loading appears to be dominated by variation in non-fossil carbon sources. These data are similar to PM 2.5 aerosol radiocarbon measurements at a suburban/rural site near Tampa, Florida [*Lewis and Stiles,* 2006] where substantial levels of biogenic carbon, 52 to 89% were measured near an urban area.

The data from Mount Rainier National Park indicate lower total and fossil aerosol carbon loadings in winter than summer. The data indicate that the contemporary carbon loading is larger than the fossil carbon loading with contemporary carbon aerosols tending to comprise a greater percentage of the total carbon loading in winter. Variation in the total carbon loading was primarily governed by variation in the contemporary carbon loading.

The Puget Sound site (Latitude: 47.5696^0, Longitude: -122.3119^0) is located next to the Beacon Hill reservoir East of interstate highway 5 (I-5) on Union Hill, in South Seattle, WA. The data indicate that this urban network site had the highest average aerosol loading as well as the highest average fossil carbon loading component of all the sites sampled during 2004/2005 and that the total, contemporary and fossil aerosol carbon loadings do not vary significantly

between the two seasons. The contemporary and fossil carbon loading fractional percentages were similar for the summer and winter field seasons.

PM 2.5 aerosol carbon loadings from Great Smoky Mountains National Park and the rural network site at the Proctor Maple Research Facility show similar trends. Total and contemporary aerosol carbon loadings are lower in winter for both sites with the contemporary carbon loading tending to comprise a greater percentage of the total carbon loading in summer. At both sites the contemporary carbon loading dominated the fossil carbon loading and variation in the total carbon loading almost completely arose from non-fossil carbon sources. Total suspended particulate and PM 10 (particles with mean mass aerodynamic diameter $\leq$ 10 μm) aerosol radiocarbon contents have been previously determined in the spring and summer of 2000 and the summer and fall of 2001 at Great Smoky Mountains National Park [*Tanner et al.,* 2004]. Although, the aerosol size fractions differ, similar to the PM 2.5 data reported here these prior radiocarbon measurements indicated that the majority of PM 10 aerosol carbon was contemporary [*Tanner et al.,* 2004].

Sites sampled during 2005/2006

The data from Grand Canyon (Hance Camp) and Rocky Mountain National Park show similar trends. Total, contemporary and fossil aerosol carbon loadings are significantly lower in the winter sampling season. The data indicate that the contemporary carbon loading is larger than the fossil carbon loading with contemporary carbon aerosols tending to comprise a greater percentage of the total carbon loading in winter. Variation in the total carbon loading was primarily governed by variation in the contemporary carbon loading.

The Phoenix site (Latitude: 33.5038^0, Longitude: -112.0958^0) is located in Maricopa County, towards the geographic center of Phoenix, AZ. The data indicate that this urban network site had the highest average total, fossil and contemporary carbon aerosol loadings of all the sites sampled during these time periods. The average total, contemporary and fossil aerosol carbon loadings were significantly higher in the winter sampling season with fossil carbon aerosols tending to comprise a greater percentage of the total carbon loading in winter.

The data from Tonto National Monument indicate that total and contemporary aerosol carbon loadings are significantly lower in winter. However, the fossil carbon loading does not vary significantly between the two sampling seasons. The data indicate that the contemporary carbon loading is larger than the fossil carbon loading and that variation in the total carbon loading almost completely arose from variation in the contemporary carbon loading.

General Trends

The ^{14}C data indicate that the contemporary and fossil aerosol loadings differ across the nine sites and suggest different percentages of carbon source inputs for the sites. The ^{14}C data also indicate a large contribution of non-fossil-carbon sources to PM 2.5 carbon at all sites, including the two urban network sites: Puget Sound and Phoenix. The two urban network sites had the highest average fossil carbon mass loadings of the nine sites. This is not unexpected considering their proximities to urban centers. Fossil carbon loadings at the two urban network sites typically comprised around half of the total PM 2.5 aerosol carbon mass loading. These fractional loading values are consistent with other ^{14}C analyses of aerosols collected at urban sampling locations in Nashville, TN [*Lewis et al.,* 2004], Zurich, Switzerland [*Szidat et al.,* 2004], Houston, TX [*Dzubay et al.,* 1982; *Lemire et al.,* 2002] and in the Los Angeles Basin, CA

[*Currie et al.,* 1983; *Berger et al.,* 1986; *Kaplan and Gordon,* 1994; *Hildemann et al.,* 1994]. Fossil carbon typically comprised approximately one-third of the total aerosol carbon collected at urban locations in Nashville, TN [*Lewis et al.,* 2004] and Zurich, Switzerland [*Szidat et al.,* 2004], averaged approximately half of the total aerosol carbon collected at urban sampling sites in Houston, TX [*Lemire et al.,* 2002] and averaged approximately two-thirds of the total aerosol carbon collected in Downtown Los Angeles, CA [*Berger et al.,* 1986].

The other seven sites (National Park and Wildlife Preserve sites together with the network site located in rural Vermont) had lower fossil carbon mass loading components than the urban sites implying a higher fraction of contemporary carbon mass in the PM 2.5 aerosols. As in prior radiocarbon studies of PM 10 aerosols collected at Great Smoky Mountains National Park [*Tanner et al.,* 2004] and PM2.5 aerosols collected at a suburban/rural site near Tampa, Florida [*Lewis and Stiles,* 2006] and a rural/forested site near Houston, Texas [*Lemire et al.,* 2002] the majority of the aerosol carbon loading at these seven sites was from contemporary carbon. For these seven non-urban sites the data indicated that variation in the total carbon mass loading was dominated by non-fossil carbon sources. At these sites trends in both fossil and contemporary carbon loading versus total PM 2.5 aerosol carbon loading are generally similar to those obtained from ^{14}C analyses of aerosols collected at Yosemite National Park, CA [*Bench and Herckes,* 2004].

Biomass burning fires and biogenic secondary organic aerosol (SOA) were thought to be the most likely sources of contemporary carbon in Houston [*Lemire et al.,* 2002]. For the Yosemite study a significant source of contemporary carbon was likely biomass burning fires [*Bench and Herckes,* 2004] while concurrent measurements of organic carbon / elemental carbon ratios in the Nashville study were consistent with biogenic secondary organic aerosols being a

significant non-fossil-fuel contributor [*Lewis et al.,* 2004]. Biogenic secondary organic aerosols were also thought to be a significant non-fossil-fuel contributor in recent work in the Southeastern US, based on Chemical Mass Balance modeling [*Zheng et al.,* 2002] and biogenic SOA tracer species [*Edney et al.,* 2003]. The ^{14}C measurements reported here cannot be used to accurately determine any contribution from biomass burning or SOA to carbon in PM 2.5 ambient aerosol at the ten sites. However, the ^{14}C measurements are consistent with an emerging view that SOA can make a significant contribution to carbon ambient aerosol and that biogenic precursors are significant contributors to the SOA.

Uncertainties in the fraction of total aerosol carbon that is contemporary carbon.

The data presented here as well as that from many prior studies have shown a sizable contribution to the total aerosol carbon loading from contemporary carbon [*Dzubay et al.,* 1982; *Currie et al.,* 1983; *Berger et al.,* 1986; *Kaplan and Gordon,* 1994; *Hildemann et al.,* 1994; *Lemire et al.,* 2002; *Bench and Herckes,* 2004; *Lewis et al.,* 2004; *Szidat et al.,* 2004; *Tanner et al.,* 2004; *Lewis and Stiles,* 2006]. Consequently, it is worthy to examine sources of uncertainty that might cause the measured contemporary carbon contents to be artificially high. The fossil and contemporary PM 2.5 aerosol carbon loadings reported here are derived using equation 2 which estimates the fraction, *Fc*, of the total aerosol carbon that is contemporary carbon. Uncertainties in *Fc* affect the accuracy of both the fossil and contemporary carbon loadings within a sample. There are five major sources of uncertainty in the estimation of *Fc*: uncertainty in the sampler operation (discussed earlier), positive and negative carbon artifacts on the filters, analytical uncertainty in the carbon isotope measurements, uncertainty in the $^{14}C/C$ ratio of the contemporary component, *Rc*, and anthroprogenic activities producing PM 2.5 aerosols

possessing elevated ^{14}C levels.

Carbon Artifact

Carbon measurements on quartz filters are subject to both positive and negative artifacts. The Hi-Vol samplers used here were not outfitted with upstream denuders to remove gas phase organic compounds. Under such a sampling setup the organic artifact will likely be dominated by a positive artifact. As shown in equation 1, the positive artifact can be corrected for by analyzing vehicle control filters, i.e., field blanks, for $^{14}C/C$ ratio and carbon mass and correcting the measured ratios and carbon mass. For this study, the median carbon loading on field blanks corresponded to 0.18 +/- 0.06 $\mu g/m^3$ with a median fraction Modern of 0.38 +/- 0.07 Modern. The FM on the vehicle control filters was always smaller than the FM on the aerosol-laden filters, so the correction always increased the aerosol FM. A previous study [*Lewis and Stiles,* 2006] found a similar result. Table 5 presents the average vehicle control filter correction to the FM of the aerosol- laden filters for each monitoring site and season. The carbon loadings on the aerosol-laden filters were usually 10 times or more larger than on the vehicle control filters, and the correction to the FM of the aerosol laden filters was frequently less than 6%. Notable exceptions are for the wintertime at Grand Canyon and Rocky Mountain National Parks where the average carbon loadings on the filter blanks were 30% and 50% of the total measured carbon loading on the aerosol-laden filters. At these sites, the corrections increased the average FM by 29% and 51%.

Analytical uncertainty in the carbon isotope measurements

The analytical uncertainty is well quantified and generally small with about 75% of the

FM data values from the PM 2.5 aerosols in the study (see tables A1 and A2) having analytical uncertainties of 5% or less. Once again, notable exceptions to this are the wintertime data at Grand Canyon and Rocky Mountain National Parks where the average analytical uncertainties in the fraction Moderns were 16% and 20%, respectively. Both sites had low wintertime carbon loadings, usually less than 0.5 $\mu g/m^3$ and these larger analytical uncertainties primarily result from subtracting the relatively large carbon contribution from the vehicle control filters.

Possible sources of variability in the fraction Modern of contemporary carbon.

Contemporary carbon in aerosol particulate matter is primarily biogenic in origin arising from the growth, destruction and anthroprogenic use of trees and plants. Surface soil (less than 1 cm deep) organics, wood smoke and SOA from biogenic gaseous precursors all contribute to the contemporary carbon aerosol loading.

^{14}C is a naturally occurring radioisotope that is produced in the atmosphere by cosmic ray neutrons. It oxidizes to CO_2, and enters the food chain through plant photosynthesis, so that all living things are "tagged" with a characteristic radiocarbon-to-total carbon ratio. Atmospheric nuclear testing produced large additional quantities of ^{14}C in the late 50's and early 60's: the radiocarbon content of the atmosphere doubled in the northern hemisphere between 1955 and 1963. Since the almost complete cessation of atmospheric testing in 1964, atmospheric ^{14}C levels have been declining as this excess is mixed into the biosphere, soils, and the ocean to the present 2006 value of ~ 1.05 Modern.

Trees and other perennial plants contain a year-by-year record of atmospheric ^{14}C in the radiocarbon content of their wood, leaves, etc. Leaves and small twigs have ^{14}C /C ratios at or close to the present atmospheric ^{14}C /C ratio. Interiors of larger branches and trees younger than

50 years - wood from closer to the time of atmospheric testing - contain more radiocarbon. Inner rings of old trees dating from before the "bomb spike" have ^{14}C /C ratios below Modern. They contain no "bomb" ^{14}C and some fraction of the natural radiocarbon they originally contained has been lost though radioactive decay. *Lewis et al.,* [2004] have used models of tree growth to estimate that the average FM of tree wood to be approximately 1.1 Modern for 10 year old trees, approximately 1.2 Modern for 30 year old trees, approximately 1.3 Modern for 50 year old trees and approximately 1.2 Modern for 75 year old trees.

Here, contemporary and fossil carbon loadings have been derived assuming R_C (the fraction Modern of contemporary carbon) = 1.08 +/- 0.06 Modern. For carbon in the form of SOA from biogenic gaseous precursors, R_C = 1.08 Modern is apt, since these precursors have ^{14}C levels that correspond to that of atmospheric CO_2 for the year of sample collection [*Lewis et al.,* 2004]. Likewise, for particulate matter carbon arising from surface soil organics (less than 1 cm), R_C = 1.08 Modern is apt, since surface soil organics have ^{14}C levels that are similar to that of atmospheric CO_2 for the year of sampling [*Trumbore,* 2000].

However, ^{14}C levels of smoke arising from wild fires or residential wood combustion will depend on the material being burned, and may even vary substantially with time as the combustion consumes large branches or logs spanning significant numbers of years of different ^{14}C activity. The majority of residential wood burning likely consumes wood grown over the past 10 to 50 years [*Szidat et al.,* 2006] while most wildfires primarily consume living foliage and fine branch wood (i.e.) recent growth over the past few decades). For most wildfires, significant quantities of bole wood from living trees are seldom consumed however, dead trees may show greater consumption especially if they have fallen over and are rotten.

For aerosols containing significant contributions from the combustion of wood grown after the mid 1950's, use of R_C = 1.08 Modern in equation 2 may result in an overestimation of the contemporary carbon component and underestimation of the fossil carbon contribution to the aerosol. Figure 3 illustrates the effects of defining R_C in equation 2 to be 1.08 Modern when a sample contains two sources of carbon - one with a FM of 0 Modern and the other with a FM of 1.3 Modern (equivalent to the average fraction Modern of wood from 50 year trees [*Lewis et al.,* 2004]). For samples with measured ^{14}C levels close to Modern, use of R_C = 1.08 Modern results in the contemporary carbon loading being overestimated by approximately 20 %.

Although, the scenario illustrated in Figure 3 is extreme many of the aerosol samples measured for this study had fraction Moderns close to unity and wood smoke from sources such as camp fires, wild fires and/or residential wood burning likely impacted several sites for at least some of the sampled time periods. Overall, Figure 3 suggests that if aerosol contemporary carbon arises solely from smoke derived from the combustion of wood grown after the mid 1950's, values of contemporary carbon reported here should be reduced by a factor of no more than about 1.3/1.08 =1.2 with a consequent correction to the fossil carbon loading.

Anthroprogenic activities producing PM 2.5 aerosols possessing elevated ^{14}C levels

Nearby anthropogenic activities such as incineration of low-level radioactive waste containing elevated levels of ^{14}C can confound radiocarbon analysis of environmental samples [*Trumbore et al.,* 2002]. High levels of ^{14}C from such sources can be readily identified by anomalously high fraction modern values, however, lower levels of contamination may not be readily identifiable. Our experience with PM 2.5 aerosols suggests that such contamination is uncommon but is also not rare. For ^{14}C aerosol apportionment analyses, sampling sites should

be judiciously selected. Locations that could be impacted by local point sources producing aerosol particulates containing highly elevated levels of ^{14}C should be avoided.

Conclusion

The fossil and contemporary carbon PM 2.5 aerosol loading data from nine IMPROVE sites reported here are based on a mass weighted apportionment and the ^{14}C determinations, by themselves, do not enable a determination of the percentage of PM 2.5 aerosol particles containing contemporary or fossil carbon. It is plausible that fossil carbon containing aerosols could comprise a small mass percentage but a significantly larger particle percentage of the PM 2.5 aerosol. Nevertheless, the ^{14}C data from the National Park and Wildlife Preserve sites reported here indicate that the mass loading of contemporary carbon aerosols dominate those from fossil carbon. This suggests that reduction of anthroprogenic sources of fossil carbon aerosols may result in little decrease in carbonaceous aerosol loading in many National Parks and rural areas.

Acknowledgments

The authors would like to thank Jan Brown for performing much of the sample preparation at LLNL. The authors would like to thank Ted Ognibene for useful discussions concerning the structure of this manuscript. This work was performed in part under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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Tables

Site Name	State	IMPROVE Code	Site Description
Brigantine National	New Jersey	BRIG1	Wildlife Preserve
Mount Rainier	Washington	MORA1	National Park
Puget Sound	Washington	PUSO 1	Urban network site
Great Smoky Mountains	Tennessee	GRSM 1	National Park
Proctor Maple Research Facility	Vermont	PMRF 1	Rural network site
Grand Canyon (Hance camp)	Arizona	HANC 1	National Park
Phoenix	Arizona	PHOE 1	Urban network site
Rocky Mountain	Colorado	ROMO 2	National Park
Tonto National Monument	Arizona	TONT 1	National Park

Table 1: Site names and state of location; IMPROVE codes for the sites and site descriptions.

More details on each site can be found at http://vista.cira.colostate.edu/improve.

	Sampler 1		Sampler 2	
Sample Time period	**fraction Modern**	**Aerosol loading ($\mu g\ m^{-3}$)**	**fraction Modern**	**Aerosol loading ($\mu g\ m^{-3}$)**
Vehicle control	0.000+/- 0.003	0.00+/-0.05	0.000+/- 0.003	0.00+/-0.05
1/4/06-1/9/06	0.517+/- 0.004	12.12 +/- 0.06	0.534+/- 0.003	11.60 +/- 0.04
1/11/06-1/16/06	0.486+/- 0.003	11.95+/- 0.06	0.501+/- 0.003	13.06+/- 0.04
1/18/06-1/23/06	0.549+/- 0.004	10.46 +/- 0.06	0.541+/- 0.003	12.13+/- 0.04
1/25/06-1/30/06	0.523+/- 0.004	10.84+/- 0.06	0.525+/- 0.003	11.70 +/- 0.04
2/1/06-2/6/06	0.522+/- 0.004	9.41+/- 0.04	0.519+/- 0.003	10.71 +/- 0.04
2/8/06-2/13/06	0.563+/- 0.004	10.72 +/- 0.04	0.556+/- 0.003	11.55 +/- 0.04
2/15/06-2/20/06	0.538+/- 0.004	8.50 +/- 0.04	0.549+/- 0.004	10.41 +/- 0.04
2/22/06-2/27/06	0.486+/-0.004	9.73 +/- 0.04	0.492+/- 0.003	10.24 +/- 0.04

Table 2: Fraction Modern and total carbon loading of PM 2.5 aerosols for each sampling period for the samplers at the Phoenix, Arizona site during January and February 2006. The uncertainties associated with the values reported are analytical uncertainties associated solely with the analytical measurement of total carbon and fraction Modern and do not account for uncertainties arising from sampler operation and/or aerosol collection. Regression analysis of the fraction Moderns of the PM 2.5 aerosols from the two samplers yields a linear least squares fit with a gradient of 1.00 and a coefficient of correlation of 0.99. Regression analysis of the total carbon loadings of the PM 2.5 aerosols from the two samplers yields a linear least squares fit with a gradient of 1.04 and a coefficient of correlation of 0.98.

Site	Contemporary versus total carbon			Fossil versus total carbon		
	Gradient	Offset	Coefficient of correlation	Gradient	Offset	Coefficient of correlation
Brigantine National Wildlife Refuge	0.85	-0.11	0.98	0.16	0.01	0.69
Mount Rainer National Park	0.75	0.18	0.98	0.26	-0.21	0.89
Puget Sound	0.51	-0.01	0.90	0.50	0.00	0.90
Great Smoky Mountains National Park	0.95	-0.17	0.98	0.05	0.16	0.24
Procter Maple Research Facility	0.92	-0.00	0.98	0.08	0.00	0.32
Grand canyon (Hance Camp)	0.95	0.02	0.95	0.05	-0.02	0.51
Phoenix	0.46	0.30	0.98	0.54	-0.33	0.98
Rocky Mountain National Park	0.87	0.01	0.99	0.13	0.01	0.91
Tonto National Monument	0.92	-0.25	0.98	0.09	0.24	0.01

Table 3: Gradients, offsets and coefficients of correlation for the linear least squares fits to contemporary and fossil carbon aerosol loadings (summer and winter combined) versus total carbon aerosol loading at each of the ten sites. Fitting the summer and winter data at a given site with separate linear curves produced lines of best fit that generally possessed similar gradients, offsets and coefficients of correlation as those obtained from a linear least squares fit to the combined seasonal data.

	Total carbon		Contemporary carbon		Fossil Carbon	
Site	**Summer average ($\mu g\ m^{-3}$)**	**Winter average ($\mu g\ m^{-3}$)**	**Summer average ($\mu g\ m^{-3}$)**	**Winter average ($\mu g\ m^{-3}$)**	**Summer average ($\mu g\ m^{-3}$)**	**Winter average ($\mu g\ m^{-3}$)**
Brigantine National Wildlife Refuge	1.6 +/- 0.5	1.6 +/- 0.7***	1.2 +/- 0.5	1.3 +/- 0.6***	0.4 +/- 0.3	0.4 +/- 0.1***
Mount Rainer National Park	2.3 +/- 1.2	1.3 +/- 0.7*	1.8 +/- 0.9	1.2 +/- 0.6**	0.5 +/- 0.3	0.1 +/- 0.1*
Puget Sound	3.8 +/- 1.7	5.0 +/- 2.1***	1.9 +/- 0.9	2.6 +/- 1.1***	1.9 +/- 0.9	2.4 +/- 1.1***
Great Smoky Mountains National Park	2.5 +/- 0.8	1.3 +/- 0.2*	2.3 +/- 0.8	1.1 +/- 0.2*	0.3 +/- 0.2	0.2 +/- 0.1***
Procter Maple Research Facility	2.1 +/- 0.6	1.4 +/- 0.5*	1.9 +/- 0.3	1.2 +/- 0.5*	0.1 +/- 0.2	0.2 +/- 0.1***
Grand canyon (Hance Camp)	2.0 +/- 1.4	0.4 +/-0.2*	1.9 +/- 0.4	0.4 +/- 0.2*	0.1 +/- 0.1	-0.01+/-0.05*
Phoenix	4.3 +/- 1.1	10.8 +/-2.4*	2.4 +/- 0.8	5.3 +/- 1.2*	1.9 +/- 0.5	5.5 +/- 1.3*
Rocky Mountain National Park	2.0 +/- 0.8	0.3 +/- 0.1*	1.7 +/- 0.7	0.3 +/- 0.1*	0.3 +/- 0.1	0.02 +/- 0.03*
Tonto National Monument	2.4 +/- 1.0	1.2 +/-0.2*	2.0 +/- 1.1	0.8 +/-0.2*	0.4 +/- 0.2	0.3 +/- 0.1***

Table 4: Average (mean +/- standard deviation) total carbon, contemporary carbon and fossil carbon loadings of the weekly PM 2.5 aerosols for both the summer and winter sampling seasons at each site, together with students t-test assessments that carbon loadings for the summer and winter sampling seasons at each site are the same. *: significance level < 0.05, **: 0.05 < significance level < 0.01, ***: significance level > 0.1.

Site	Season	% FM correction
Brigantine National Wildlife Refuge	Summer	4.3
	*Winter	4.8
Mount Rainer National Park	Summer	7.0
	*Winter	12.4
Puget Sound	Summer	1.1
	Winter	1.2
Procter Maple Research Facility	Summer	4.5
	Winter	5.2
Great Smoky Mountains National Park	Summer	2.4
	Winter	6.4
Grand canyon (Hance Camp)	Summer	7.0
	Winter	28.9
Rocky Mountain National Park	Summer	8.0
	Winter	51.3
Tonto National Monument	Summer	3.2
	Winter	10.8
Phoenix	**Summer	2.7
	Winter	0.9

Table 5: Percent increase in the FM of the aerosol-laden filters after correction for positive carbon artifact from the vehicle control filters. *Summer field vehicle control filters were used in place of uncollected winter vehicle control filters. **Winter vehicle control filters were used in place of uncollected summer vehicle control filters.

Figure Captions

Figure 1: Location of the nine IMPROVE network sites.

Figure 2: Graphs of contemporary and fossil carbon loading versus total carbon loading for PM 2.5 aerosols at the nine sites. The dashed and solid lines are linear least squares fits to the contemporary and fossil carbon data, respectively (summer and winter combined). A) Brigantine National Wildlife Refuge (Data from 7/28/04 to 8/2/04 are not included owing to the outlying FM value.); B) Mount Rainier National Park; C) Puget Sound; D) Great Smoky Mountains National Park; E) Proctor Maple Research Facility; F) Grand canyon (Hance Camp); G) Phoenix; H) Rocky Mountain National Park; I) Tonto National Monument.

Figure 3: Contemporary and fossil carbon fractional loadings derived using equation 2 with R_C =1.08 Modern and R_C = 1.3 Modern for a sample consisting two sources of carbon - one with a FM of 0 Modern and the other with a FM of 1.3 Modern. The values on the x-axis correspond to actual fraction Moderns of various mixtures of the two components.

Figures

Figure 1:

Figure 2:

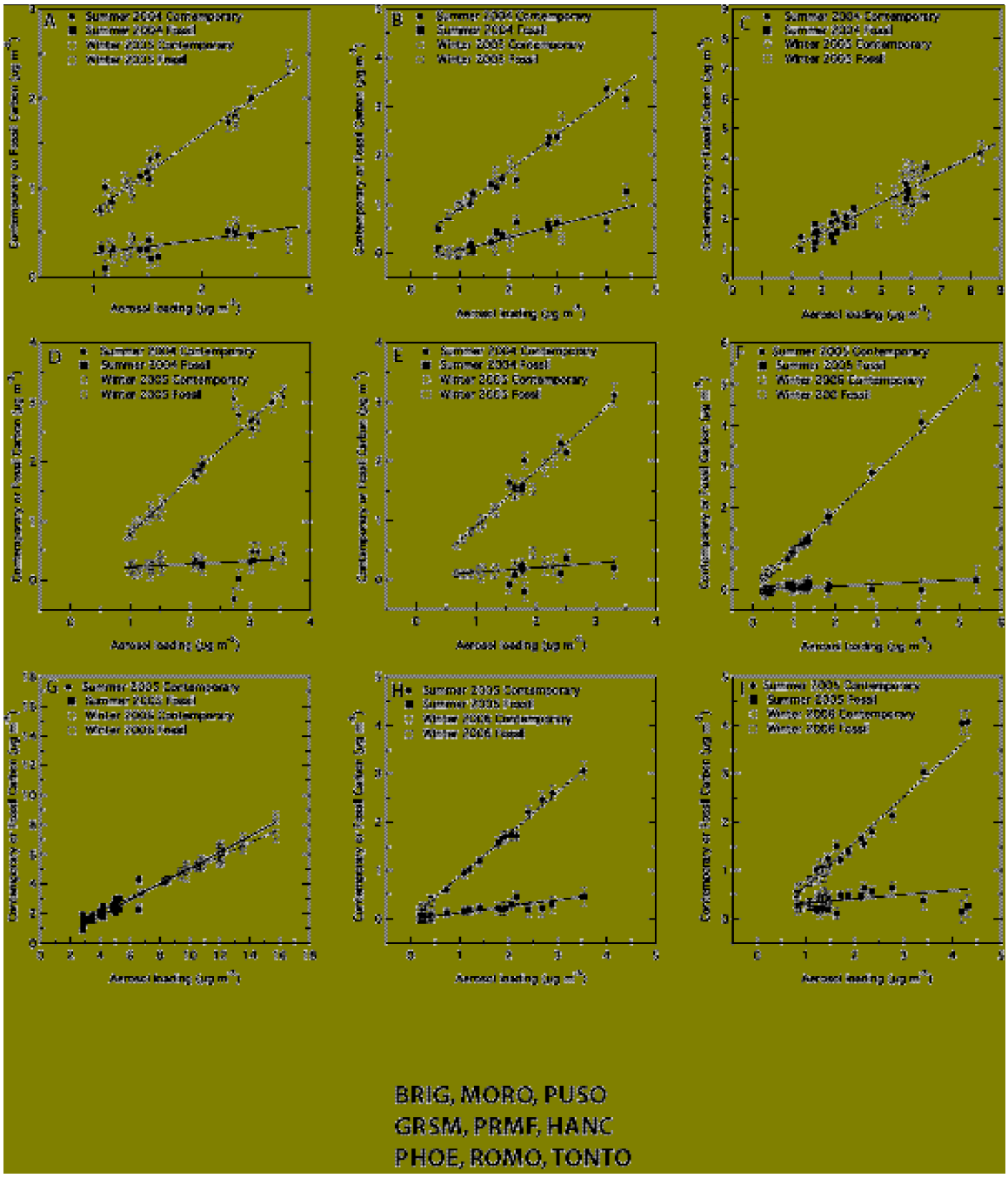
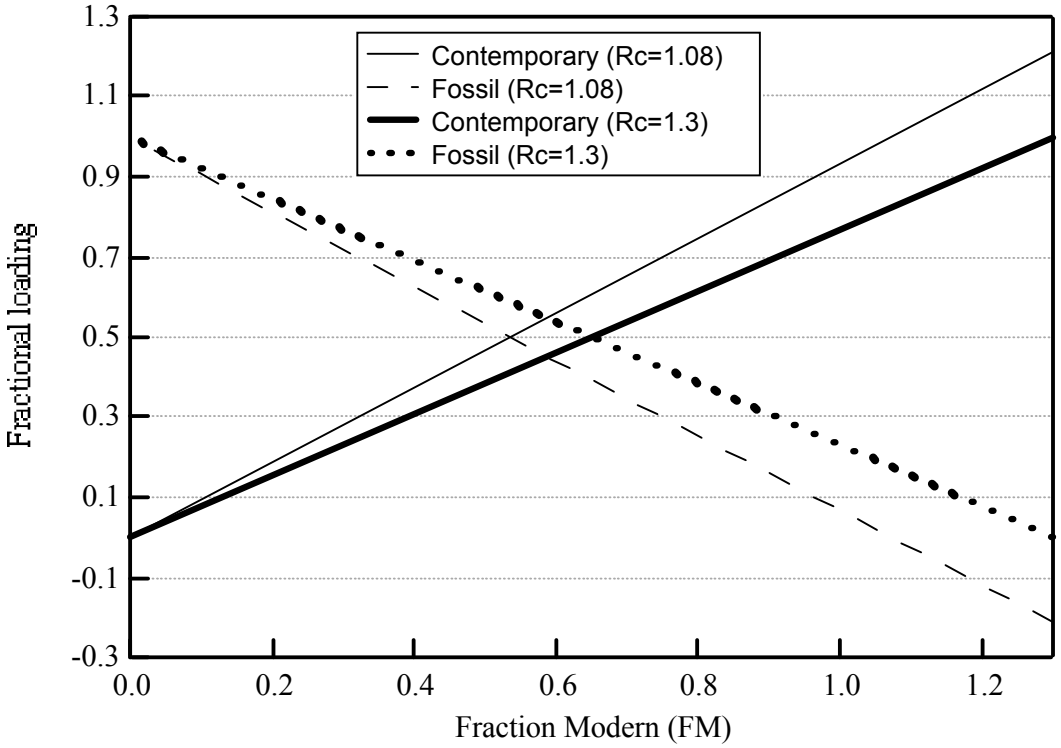


Figure 3:


Contemporary (Rc=1.08)
Fossil (Rc=1.08)
Contemporary (Rc=1.3)
Fossil (Rc=1.3)
Fractional loading
Fraction Modern (FM)
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
-0.3
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Auxiliary Material

	Brigantine National Wildlife Refuge		Mount Rainier National Park		Puget Sound		Great Smoky Mountains National Park		Proctor Maple Research Facility	
Sample Time period	fraction Modern	Aerosol loading (μg m^{-3})	fraction Modern	Aerosol loading (μg m^{-3})	fraction Modern	Aerosol loading (μg m^{-3})	fraction Modern	Aerosol loading (μg m^{-3})	fraction Modern	Aerosol loading (μg m^{-3})
6/2/04 - 6/7/04	0.853 +/- 0.029	1.43 +/- 0.04	0.753 +/- 0.058	2.155 +/- 0.04	0.605 +/- 0.012	2.75 +/- 0.04	0.909 +/- 0.016	3.04 +/- 0.04	1.142 +/- 0.041	1.55 +/- 0.04
6/9/04 - 6/14/04	0.922 +/- 0.028	1.59 +/- 0.04	0.930 +/- 0.072	0.559 +/- 0.04	0.639 +/- 0.014	2.31 +/- 0.04	0.963 +/- 0.016	3.05 +/- 0.04	NVS	NVS
6/16/04 - 6/21/04	0.855+/- 0.027	1.50 +/- 0.04	0.897 +/- 0.025	2.836 +/- 0.04	0.633 +/- 0.006	6.06 +/- 0.04	0.935 +/- 0.022	2.15 +/- 0.04	NVS	NVS
6/23/04 - 6/28/04	0.785 +/- 0.025	1.52 +/- 0.04	0.932 +/- 0.027	1.631 +/- 0.04	0.614 +/- 0.010	3.32 +/- 0.04	0.903 +/- 0.022	2.08 +/- 0.04	0.970 +/- 0.031	1.78 +/- 0.04
6/30/04 - 7/5/04	0.939 +/- 0.030	1.52+/- 0.04	0.875 +/- 0.022	1.872 +/- 0.04	0.589 +/- 0.011	2.85 +/- 0.04	0.966 +/- 0.022	2.20 +/- 0.04	NVS	NVS
7/7/04 - 7/12/04	0.778 +/- 0.031	1.17+/- 0.04	NVS	NVS	0.607 +/-0.009	3.53 +/- 0.04	0.948 +/- 0.022	2.20 +/- 0.04	1.036 +/- 0.025	2.40 +/- 0.04
7/14/04 - 7/19/04	NVS	NVS	0.857 +/- 0.015	2.807 +/- 0.04	0.596 +/- 0.008	3.81 +/- 0.04	0.943 +/- 0.014	3.55 +/- 0.04	NVS	NVS
7/21/04 - 7/26/04	0.881 +/- 0.018	2.46 +/- 0.04	0.850 +/- 0.014	2.999 +/- 0.04	0.588 +/- 0.006	5.82 +/- 0.04	0.962 +/- 0.015	3.37 +/- 0.04	1.018 +/- 0.018	3.31 +/- 0.04
7/28/04 - 8/2/04	0.302 +/- 0.009	1.56 +/- 0.04	0.909 +/- 0.012	4.011 +/- 0.04	0.551 +/- 0.005	5.90 +/- 0.04	0.934 +/- 0.023	2.05 +/- 0.04	1.203 +/- 0.038	1.80 +/- 0.04
8/4/04 - 8/9/04	0.835 +/- 0.018	2.31 +/- 0.04	0.907 +/- 0.034	1.218 +/- 0.04	0.465 +/- 0.006	4.09 +/- 0.04	0.920 +/- 0.015	3.14 +/- 0.04	1.025 +/- 0.035	1.64 +/- 0.04
8/11/04 - 8/16/04	0.758 +/- 0.034	1.06 +/- 0.04	0.772 +/- 0.009	4.403 +/- 0.04	0.458 +/- 0.004	6.51 +/- 0.04	1.071 +/- 0.019	2.81 +/- 0.04	0.952 +/- 0.032	1.66 +/- 0.04
8/18/04 - 8/23/04	0.832 +/- 0.018	2.25 +/- 0.04	0.829 +/- 0.023	1.750 +/- 0.04	0.383 +/- 0.006	3.41 +/- 0.04	0.972 +/- 0.017	3.00 +/- 0.04	0.924 +/- 0.021	2.51 +/- 0.04
8/25/04 - 8/30/04	0.987 +/- 0.042	1.11 +/- 0.04	1.047 +/- 0.038	1.267 +/- 0.04	0.378 +/- 0.007	2.75 +/- 0.04	1.208 +/- 0.022	2.73 +/- 0.04	0.942 +/- 0.030	1.76 +/- 0.04
12/1/04-12/6/04	NVS	NVS	1.046 +/- 0.059	0.788 +/- 0.04	0.588 +/- 0.008	4.04 +/- 0.04	0.876 +/- 0.032	1.36 +/- 0.04	0.966 +/- 0.049	0.91 +/- 0.04
12/8/04-12/13/04	NVS	NVS	1.098 +/- 0.053	0.942 +/- 0.04	0.534 +/- 0.010	2.72 +/- 0.04	0.971 +/- 0.049	1.07 +/- 0.04	0.921 +/- 0.063	0.67 +/- 0.04
12/15/04-12/20/04	NVS	NVS	1.023 +/- 0.041	1.141 +/- 0.04	0.488 +/- 0.005	6.33 +/- 0.04	0.881 +/- 0.029	1.53 +/- 0.04	0.918 +/- 0.043	1.04 +/- 0.04
12/22/04-12/27/04	NVS	NVS	1.032 +/- 0.028	1.725 +/- 0.04	0.667 +/- 0.008	4.87 +/- 0.04	0.871 +/- 0.034	1.29 +/- 0.04	0.950 +/- 0.033	1.64 +/- 0.04
12/29/04-1/3/05	NVS	NVS	1.080 +/- 0.050	0.992 +/- 0.04	0.694 +/- 0.007	5.82 +/- 0.04	0.954 +/- 0.032	1.52 +/- 0.04	NVS	NVS
1/5/05-1/10/05	0.747 +/- 0.031	1.14 +/- 0.04	1.088 +/- 0.062	0.781 +/- 0.04	0.642 +/- 0.006	5.70 +/- 0.04	0.908 +/- 0.044	0.99 +/- 0.04	0.929 +/- 0.034	1.33 +/- 0.04
1/12/05-1/17/05	0.854 +/- 0.034	1.18 +/- 0.04	NVS	NVS	0.616 +/- 0.011	2.98 +/- 0.04	0.841 +/- 0.028	1.47 +/- 0.04	0.914 +/- 0.042	1.12 +/- 0.04
1/19/05-1/24/05	0.905 +/- 0.033	1.29 +/- 0.04	1.032 +/- 0.074	0.612 +/- 0.04	0.457 +/- 0.004	6.02 +/- 0.04	0.909 +/- 0.033	1.36 +/- 0.04	0.957 +/- 0.036	2.14 +/- 0.04
1/26/05-1/31/05	0.820 +/- 0.018	2.32 +/- 0.04	1.057 +/- 0.049	0.988 +/- 0.04	0.463 +/- 0.004	6.29 +/- 0.04	0.804 +/- 0.037	1.04 +/- 0.04	0.969 +/- 0.035	2.30 +/- 0.04
2/2/05-2/7/05	0.923 +/- 0.017	2.81 +/- 0.04	1.085 +/- 0.051	0.980 +/- 0.04	NVS	NVS	0.777 +/- 0.025	1.50 +/- 0.04	0.839 +/- 0.021	1.95 +/- 0.04
2/9/05-2/14/05	0.735 +/- 0.026	1.35 +/- 0.04	1.033 +/- 0.041	1.177 +/- 0.04	0.575 +/- 0.006	5.46 +/- 0.04	0.933 +/- 0.039	1.15 +/- 0.04	0.961 +/- 0.057	0.78 +/- 0.04
2/16/05-2/21/05	0.841 +/- 0.030	1.34 +/- 0.04	0.979 +/- 0.016	3.089 +/- 0.04	0.661 +/- 0.006	6.03 +/- 0.04	0.824 +/- 0.044	0.97 +/- 0.04	1.007 +/- 0.064	1.07 +/- 0.04
2/23/05-2/28/05	NVS	NVS	0.975 +/- 0.023	2.032 +/- 0.04	0.517 +/- 0.005	8.35 +/- 0.04	1.005 +/- 0.037	1.33 +/- 0.04	0.998 +/- 0.045	1.30 +/- 0.04

Table A1: Fraction Modern and total carbon loading of PM 2.5 aerosols for each sampling period for each of the five sites sampled in the summer of 2004 and the winter of 2004/2005. Values have been corrected for carbon contribution from vehicle control filters. At some of the sites there were periods when the sampler did not operate due to power or hardware failures or periods when sampling was not correctly performed owing to improper sampler setup. Such periods are marked as no viable sample (NVS). The uncertainties associated with the values reported are analytical uncertainties associated solely with the analytical measurement of total carbon and fraction Modern and do not account for uncertainties arising from sampler operation.

	Grand Canyon (Hance camp		Phoenix		Rocky Mountain National Park		Tonto National Monument	
Sample Time period	fraction Modern	Aerosol loading ($\mu g\ m^{-3}$)	fraction Modern	Aerosol loading ($\mu g\ m^{-3}$)	fraction Modern	Aerosol loading ($\mu g\ m^{-3}$)	fraction Modern	Aerosol loading ($\mu g\ m^{-3}$)
6/1/05-6/8/05	0.965 +/- 0.081	1.36 +/- 0.11	0.600 +/- 0.013	3.52 +/- 0.06	0.889 +/- 0.071	0.73 +/- 0.05	0.777 +/- 0.025	1.70 +/- 0.04
6/8/05-6/13/05	0.996 +/- 0.075	1.26 +/- 0.09	0.639 +/- 0.011	4.20 +/- 0.06	0.925 +/- 0.051	1.09 +/- 0.05	0.771 +/- 0.020	2.19 +/- 0.04
6/15/05-6/20/05	0.943 +/- 0.066	1.35 +/- 0.09	0.6172 +/- 0.009	5.27+/- 0.06	0.860 +/- 0.024	2.16 +/- 0.05	0.838 +/- 0.022	2.14 +/- 0.04
6/22/05-6/27/05	1.032 +/- 0.071	1.33 +/- 0.09	0.642 +/- 0.006	5.03 +/- 0.03	0.995 +/- 0.026	2.40 +/- 0.05	1.016 +/- 0.014	4.32 +/- 0.04
6/29/05-7/4/05	1.082 +/- 0.026	4.08 +/- 0.09	NVS	NVS	0.957 +/- 0.030	1.93 +/- 0.05	0.834 +/- 0.017	2.77 +/- 0.04
7/6/05-7/11/05	1.026 +/- 0.053	1.85 +/- 0.09	0.578 +/- 0.009	4.82 +/- 0.06	0.995 +/- 0.030	2.68 +/- 0.05	0.827 +/- 0.020	2.35 +/- 0.04
7/13/05-7/18/05	1.033 +/- 0.019	5.41 +/- 0.09	0.700 +/- 0.008	6.57 +/- 0.06	0.935 +/- 0.017	3.53 +/- 0.05	0.961 +/- 0.016	3.41 +/- 0.04
7/20/05-7/25/05	1.076 +/- 0.036	2.87 +/- 0.09	0.7450 +/- 0.018	2.81 +/- 0.06	0.971 +/- 0.021	2.89 +/- 0.05	1.040 +/- 0.014	4.20 +/- 0.04
7/27/05-8/1/05	1.024 +/- 0.082	1.18 +/- 0.09	0.613 +/- 0.015	2.86 +/- 0.06	0.919 +/- 0.027	2.05 +/- 0.05	1.004 +/- 0.034	1.63 +/- 0.04
8/3/05-8/8/05	1.042 +/- 0.104	0.94 +/- 0.09	0.492 +/- 0.009	4.00 +/- 0.06	0.965 +/- 0.031	1.88 +/- 0.05	0.895 +/- 0.037	1.32 +/- 0.04
8/10/05-8/15/05	1.078 +/- 0.057	1.81 +/- 0.09	0.528 +/- 0.012	3.20 +/- 0.06	0.953 +/- 0.032	1.79 +/- 0.05	0.909 +/-0.041	1.21 +/- 0.04
8/17/05-8/22/05	0.991 +/- 0.094	1.00 +/- 0.09	0.523 +/- 0.009	4.17 +/- 0.06	0.918 +/- 0.046	1.20 +/- 0.05	0.941 +/- 0.035	1.45 +/- 0.04
8/24/05-8/29/05	0.947 +/- 0.105	0.85 +/- 0.09	0.549 +/- 0.008	5.09 +/- 0.06	0.921 +/- 0.039	1.41 +/- 0.05	0.799 +/- 0.023	1.88 +/- 0.04
11/30/05-12/5/05	1.515+/-0.259	0.30+/-0.05	0.537+/-0.007	6.74+/-0.06	1.051+/-0.143	0.41+/-0.05	0.792+/-0.055	1.08+/-0.07
12/7/05-12/12/05	1.239+/-0.212	0.30+/-0.05	0.565+/-0.003	13.52+/-0.04	1.015+/-0.231	0.24+/-0.05	0.826+/-0.042	1.48+/-0.07
12/14/05-12/19/05	1.219+/-0.144	0.44+/-0.05	0.543+/-0.005	8.28+/-0.06	0.991+/-0.132	0.42+/-0.05	0.965+/-0.056	1.29+/-0.07
12/21/05-12/26/05	0.990+/-0.429	0.11+/-0.05	0.499+/-0.003	15.76+/-0.06	0.976+/-0.187	0.29+/-0.05	0.825+/-0.073	0.83+/-0.07
12/28/05-1/2/06	1.075+/-0.151	0.37+/-0.05	0.585+/-0.004	12.07+/-0.06	1.072+/-0.230	0.26+/-0.05	0.674+/-0.061	0.81+/-0.07
1/4/06-1/9/06	1.082+/-0.142	0.40+/-0.05	0.517+/-0.004	12.12+/-0.06	1.084+/-0.317	0.19+/-0.05	0.784+/-0.064	0.90+/-0.07
1/11/06-1/16/06	0.937+/-0.079	0.63+/-0.05	0.486+/-0.003	11.95+/-0.06	1.039+/-0.223	0.26+/-0.05	0.735+/-0.038	1.45+/-0.07
1/18/06-1/23/06	0.975+/-0.157	0.32+/-0. 05	0.548+/-0.004	10.46+/-0.06	NVS	NVS	0.776+/-0.053	1.09+/-0.07
1/25/06-1/30/06	1.044+/-0.115	0.48+/-0.05	0.523+/-0.004	10.84+/-0.06	1.083+/-0.232	0.26+/-0.05	0.761+/-0.041	1.40+/-0.07
2/1/06-2/6/06	1.289+/-0.280	0.23+/-0.05	0.522+/-0.004	9.41+/-0.04	1.045+/-0.263	0.20+/-0.05	0.684+/-0.033	1.26+/-0.05
2/8/06-2/13/06	1.145+/-0.220	0.26+/-0.05	0.563+/-0.004	10.72+/-0.04	1.106+/-0.308	0.18+/-0.05	0.755+/-0.043	1.07+/-0.05
2/15/06-2/20/06	1.024+/-0.055	1.05+/-0.05	0.538+/-0.004	8.50+/-0.04	1.003+/-0.123	0.42+/-0.05	0.727+/-0.035	1.28+/-0.05
2/22/06-2/27/06	1.132+/-0.149	0.39+/-0.05	0.486+/-0.004	9.73+/-0.04	0.798+/-0.096	0.43+/-0.05	0.638+/-0.029	1.37+/-0.05

Table A2: Fraction Modern and total carbon loading of PM 2.5 aerosols for each sampling period for each the four sites sampled in the summer of 2005 and the winter of 2005/2006. Values have been corrected for carbon contribution from vehicle control filters. At some of the sites there were periods when the sampler did not operate due to power or hardware failures or periods when sampling was not correctly performed owing to improper sampler setup. Such periods are marked as no viable sample (NVS). The uncertainties associated with the values reported are analytical uncertainties associated solely with the analytical measurement of total carbon and fraction Modern and do not account for uncertainties arising from sampler operation.